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Visible Light Emitting Materials and Injection Devices

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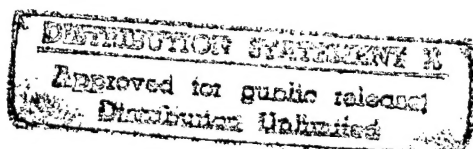
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(I) **Growth by MBE and Characterization of Widegap II-VI and Column III-Nitride Materials (Robert Park)**

A. II-VI Semiconductors

- Low temperature *in situ* substrate cleaning technique developed for MBE employing a remotely generated atomic hydrogen beam.
- GaAs wafers cleaned at 300 C.
- A strong correlation was found between the free-hole concentration in p-type ZnSe:N and the cathodoluminescence intensity recorded during epilayer growth by MBE.
- Growth parameter optimization for deposition of doped epilayers via real-time *in-situ* CL intensity monitoring.
- Structural defects at wide-gap II-VI/GaAs hetero-interfaces shown to act as laser light scatterers using an *in situ* laser beam probe during epilayer growth by MBE.
- Potential application to real-time *in situ* monitoring of lattice-matched epitaxy.
- Time-resolved measurements of photo-pumped lasing in ZnCdSe/ZnSe MQW cavities in collaboration with Dr. Robert Taylor (University of Oxford) - both low- and high-threshold carrier density laser cavities examined.
- Observations consistent with a gain mechanism involving localized excitons when lasing occurs at low carrier densities, but at high carrier densities gain mechanism involves stimulated recombination from a correlated electron-hole plasma.
- *Ex situ* UV-ozone treatments and *in situ* atomic hydrogen treatments were optimized for Sumitomo ZnSe wafers.
- Atomically-smooth, contamination-free ZnSe wafer surfaces produced at 300°C for subsequent ZnSe homoepitaxy studies.
- Homoepitaxial growth of MQW active region LED structure and etching of epilayer system to produce a mesa structure was demonstrated.
- A CdZnSe/ZnSe MQW active region green LED device (see Fig. I.1) was grown and fabricated on a Sumitomo ZnSe wafer. The EL peak showed a linewidth of 9.9 nm at RT, the peak wavelength for the particular device being 508 nm (see Fig. I.2).
- Determined that the surface stoichiometry maintained during the first five monolayers of ZnSe epitaxial growth can have a significant influence on the stacking fault concentration in 2 μm thick homoepitaxial layers.

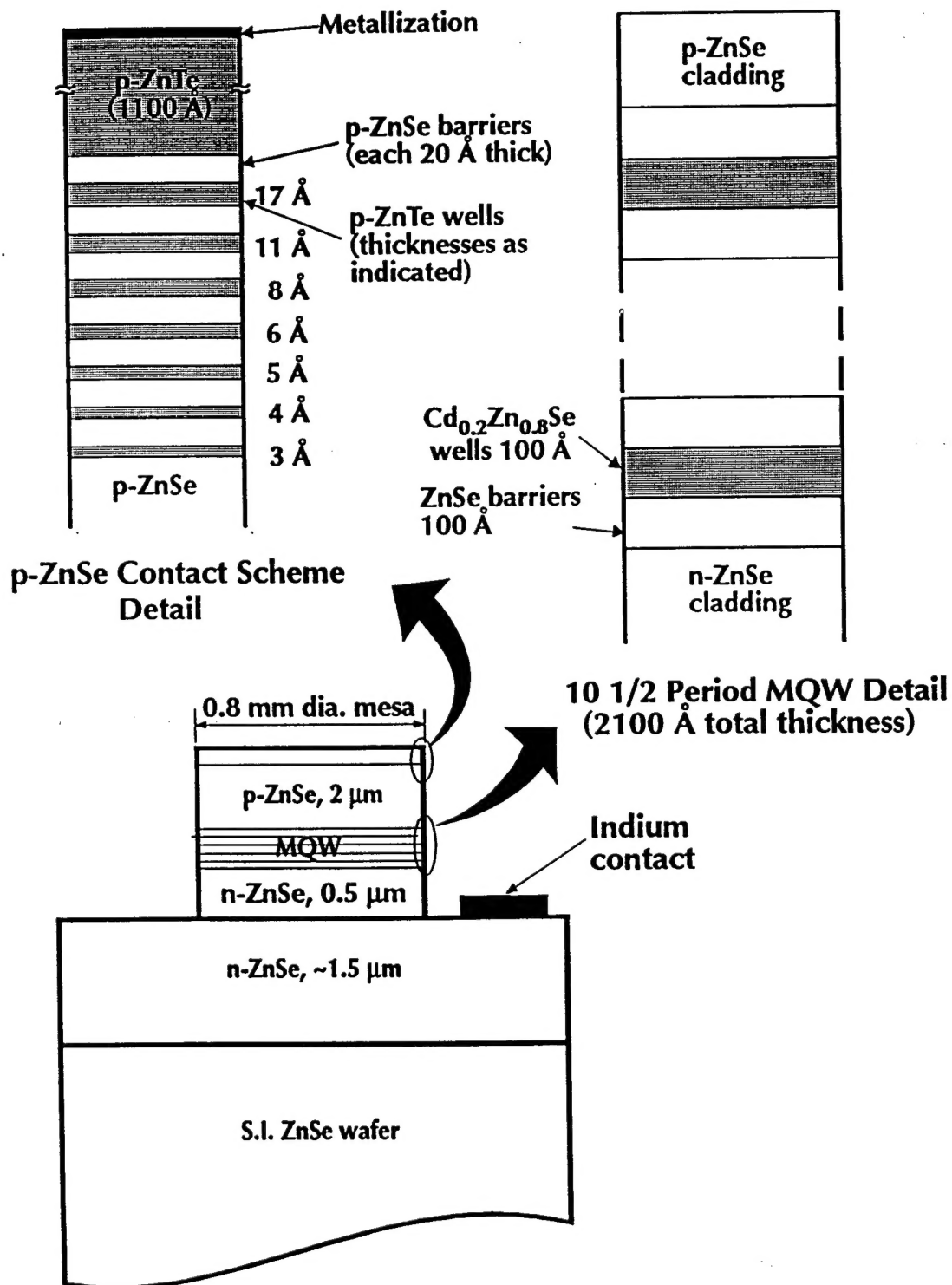


Fig. I.1.



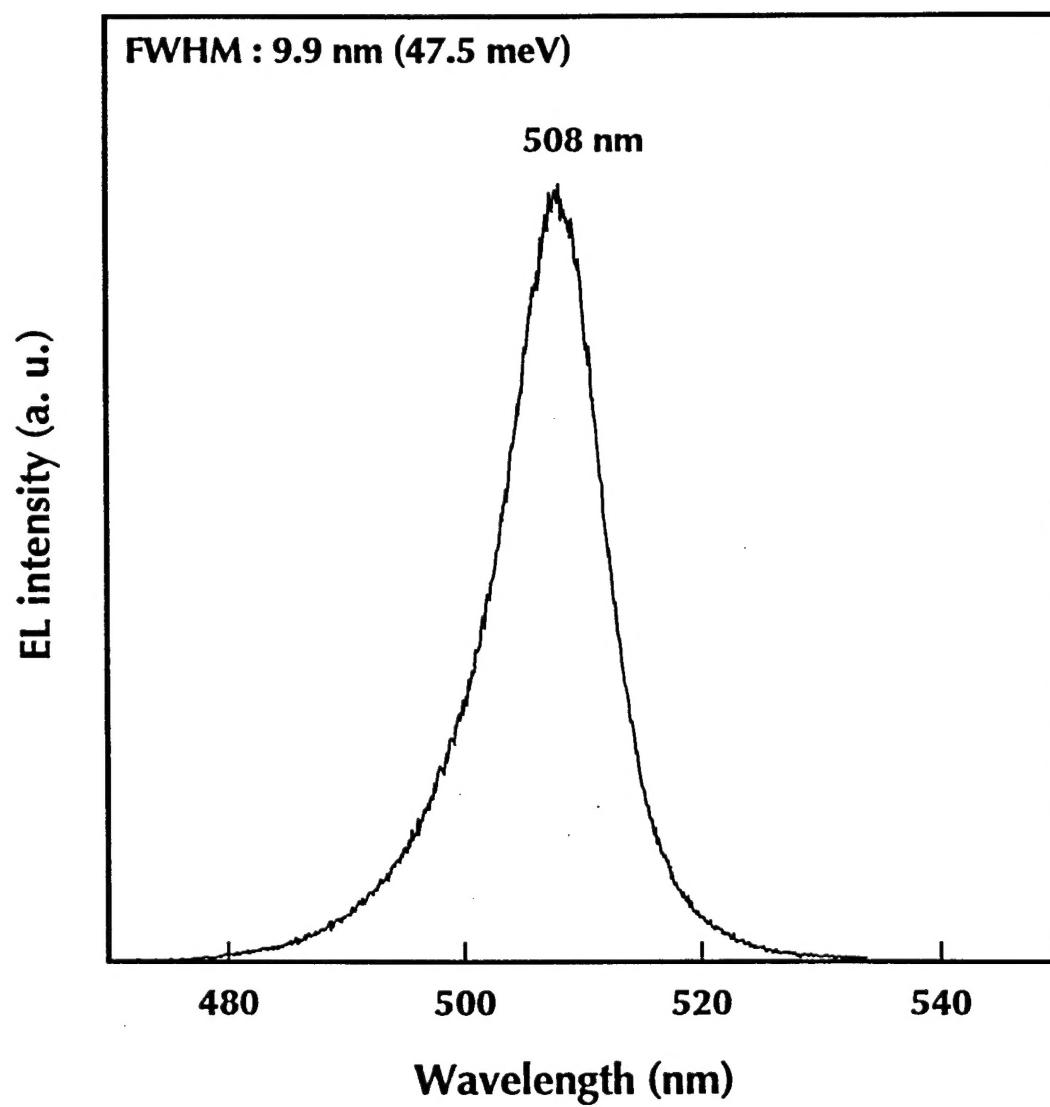


Fig. I.2.

- We have been able to minimize the stacking fault concentration to a level in the  $10^4 \text{ cm}^{-2}$  range (comparable to the stacking fault concentration in the ZnSe substrates used for epitaxy) by appropriate selection of a delay time ( $\sim 30 \text{ s}$  for a substrate temperature of  $300 \text{ C}$ ) employed during an alternate element (Zn and Se) exposure phase of growth. The delay time in question is the time elapsed between closing the Se shutter and opening the Zn shutter. We have shown that the surface stoichiometry (Zn to Se atomic ratio) can be tailored during the delay phase since Se thermal desorption occurs at the growth temperature in a controlled fashion from an initially Se-terminated surface, and, it is postulated that selection of an optimum delay time corresponding to the attainment of a near-stoichiometric surface results in the growth of low stacking fault concentration material.

#### B. Column III-Nitride Semiconductors

- Showed the feasibility of employing an rf plasma discharge unit as a source of reactive nitrogen atoms to grow epitaxial column III-nitrides.
- The rf plasma source approach is now used around the world to grow GaN and related alloys epitaxially by MBE.
- Demonstrated the growth of zincblende-GaN films on  $\text{-SiC}$  coated (001) Si substrates by rf-plasma MBE.
- Unintentionally-doped zincblende films had a carrier concentration of  $6 \times 10^{17} \text{ cm}^{-3}$  and a mobility value of  $760 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at RT.
- n-type carrier concentrations in the range  $10^{18} - 3 \times 10^{20} \text{ cm}^{-3}$  were produced by Si-doping during MBE growth.
- Demonstrated the growth of wurtzite-GaN films on sapphire substrates by rf-plasma MBE.
- Unintentionally-doped wurtzite-GaN films were semi-insulating when an AlN buffer layer was incorporated (otherwise the unintentionally-doped films were  $10^{18} \text{ cm}^{-3}$  n-type).
- n-type carrier concentrations in the range,  $10^{17} - 10^{20} \text{ cm}^{-3}$  were produced by Si-doping during MBE growth.
- The kinetics of growth of GaN/(0001) sapphire heteroepitaxial films were examined in the relatively-low substrate temperature range,  $560$  to  $640 \text{ C}$ , using the reflection high energy electron diffraction (RHEED) specular reflection intensity monitoring technique. In particular, an alternate element exposure method of growth was employed in which Ga and N atoms were supplied separately (rather than simultaneously, as in conventional molecular beam epitaxy (MBE)) to the substrate with the inclusion of a time delay

between successive Ga flux and N flux exposures. We interpret the observed time dependent recovery of the RHEED specular reflection intensity during the time delay phases to be associated with Ga-N surface molecule migration on Ga-terminated surfaces and the activation energy for this migration process was determined to be  $1.45 \pm 0.25$  eV.

- The photoluminescence (PL) characteristics of epilayers grown by the alternate element exposure method and by conventional MBE at the same growth temperature were compared. Based on the PL and RHEED analysis, it is speculated that the source of the yellow-band luminescence in defective GaN epilayers is electron-hole pair recombination at positively-charged Ga interstitials local to edge-dislocations.

### (II) Growth and processing of Nitrides (Cammy Abernathy and Steve Pearton)

The main conclusions of our two year project (1995-1997) were:

- (i) C produces compensated p-type doping of GaN under MOMBE conditions, with maximum hole concentrations of  $3 \times 10^{17} \text{ cm}^{-3}$ .
- (ii) C, O, H background impurity levels all decrease with growth temperature, and material quality measured by XRD improves with growth temperature.
- (iii) InGaN produced extremely good contact resistance for n-type GaN, with W-based contacts having  $\rho_c$  values  $< 10^{-6} \text{ ohm-cm}^2$ . These are stable to  $\sim 500^\circ\text{C}$  for InN, and to  $\sim 800^\circ\text{C}$  for  $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ .
- (iv) a new selective wet etch for AlN over GaN was identified (KOH). The etch rates are exponentially dependent on temperature and inversely dependent on material quality.
- (v) achieved first n- and p-doping of GaN by ion implantation.
- (vi) first GaN JFET fabricated.
- (vii) first Ca-doping to form p-GaN.
- (viii) established reactivation mechanism in electron-beam irradiated p-GaN, i.e. minority carrier enhanced debonding of H.
- (ix) determined process modules in which H indiffusion occurs in GaN, and the thermal stability of this effect.
- (x) developed implant isolation processes for GaN, InGaN, InAlN.
- (xi) established thermal stability of all nitrides during annealing and temperatures at which N loss occurs. Developed AlN cap for preventing dissociation of GaN during annealing.
- (xii) developed etch processes (ECR, ICP) with 5 times faster rates than previously achieved.
- (xiii) first epitaxial Er-doping of nitrides.
- (xiv) developing grating process for GaN, InGaN.

### (III) Ohmic Contacts to p-ZnSe, p-ZnTe and p-GaN (Paul Holloway, John Fijol and Jeff Trexler)

#### a) p-ZnSe:

The electrical properties and structure of three different electrical contacts to p-ZnSe were studied. Sputter deposited Au and Ag contacts were heat treated over a range of 150 to 400°C to determine the effect of heat treatments on the reverse bias breakdown voltage of these Schottky contacts. The minimum breakdown voltage for Au contacts was found to be ~3 volts following heat treatment at 350°C for 30 minutes. Analytical data indicated that Au diffused into the ZnSe during heat treatment, resulting in the formation of deep acceptor levels which led to defect assisted avalanche breakdown dominating conduction. The minimum reverse bias breakdown voltage for Ag contacts was found to be 2.3 volts following heat treatment at 150°C for 45 minutes. Analytical data indicated that oxygen was incorporated at the Ag/ZnSe interface during deposition and heat treatment which co-doped the surface region of the ZnSe and led to field emission dominating conduction.

The electrical properties and conduction mechanisms of HgSe/p-ZnSe contacts were also studied. These contacts were formed by a novel *ex situ* process which involved capping the ZnSe with amorphous Se, diffusion of Hg into the Se to form a solid solution, and precipitation of HgSe from solution. Auger, secondary ion mass spectrometry and transmission electron microscopy showed that this process yielded a stoichiometric HgSe layer with regions epitaxed to the underlying ZnSe. Temperature dependent measurements showed that the valence band offset between HgSe and ZnSe was 0.55 eV.

The degradation of ZnTe/ZnSe multiquantum well contacts under high current loading (1000 to 1500 A/cm<sup>2</sup>) were also studied. Localized temperatures during degradation was measured to be 300°C or greater at the point where electrical power was supplied. Auger data from degraded samples indicated that due to the localized heating, Zn and Te from the ZnTe layers and Zn from the ZnSe layers diffused through the Au metallization to the sample surface. In addition, thermal stress from the localized heating generated micro-cracks in the ZnSe which acted as high diffusivity paths for impurities. Rectangular defects oriented to the micro-cracks had similar geometries to dislocation patches (dark line defects) which form in the quantum well region of degraded ZnSe based laser devices. This suggests the formation of similar dislocation patches in the quantum well region of the multiquantum well contacts.

#### b) p-ZnTe

This work consisted of the formation and characterization of electrical contacts to p-ZnTe and p-GaN. Formation of ohmic contacts to  $3 \times 10^{18}$  cm<sup>-3</sup> nitrogen doped p-ZnTe by sputter deposition of Au films (150 nm thick) was demonstrated. The as-deposited contacts had rectifying I-V characteristics which became linear upon heat treating to 200°C for 15 minutes in flowing forming gas (10% H<sub>2</sub>, 90% N<sub>2</sub>). This ohmic behavior was attributed to Au diffusion into the near-surface layer of the p-ZnTe, where it behaved as an acceptor. AES and SIMS verified that Au diffused into the near surface region without formation of interfacial phases. A maximum current density of 2.3 A/cm<sup>2</sup> at 5 V was measured following a 250°C, 15 minute heat treatment. Upon heating to 350 °C, Au diffusion was much more extensive and resulted in compound formation at the interface as was evident from AES and SIMS depth profiles. Extensive diffusion and/or compound formation led to severe degradation of the electrical properties of the Au/ZnTe contacts.

c) p-GaN

For ohmic contacts to p-GaN, a variety of contact schemes were investigated. Sputter deposited Au contacts (240 nm) were rectifying as-deposited and remained so for heat treatments up to 600 °C. AES depth profiles showed that no Au/GaN reaction took place either during deposition or heating to 600 °C.

For electron beam evaporated Ni/Au contacts (50 nm/100 nm) heating to 400 °C for 5 minutes in flowing N<sub>2</sub> resulted in nearly linear I-V curves. AES depth profiles showed widespread diffusion of Ni through the Au capping layer to the surface. Heating to 600 °C for 5 minutes led to dissociation of the GaN due to reactions with Ni. This was evidenced because Ga diffused to the surface of the contact. It was postulated that Ni dissociation of the GaN lattice led to ohmic contacts because of doping of the surface by C, a known acceptor in GaN, due to adventitious interfacial contamination. A C layer (10 nm) intermediate between the Au and Ni layers was added to try to take further advantage of the GaN dissociation and to increase the interface doping concentration. This was unsuccessful, probably due to the fact that the deposited C was bound in ring structures as opposed to chains, which is the form of C which has been incorporated as dopant.

Contacts of Pd/Au (50 nm/100 nm) resulted in rectifying I-V characteristics both as deposited and after all heat treatment conditions, with the best results being obtained following a 900 °C, 15 sec RTA treatment in N<sub>2</sub>. Following this heat treatment, AES depth profiles showed Pd had diffused into the Au capping layer where a Pd-Au phase was formed throughout the entire contact layer. There was no evidence of GaN dissociation in these samples.

Contacts of Cr/Au (50 nm/100 nm) were the final scheme investigated. Ohmic contacts were formed following a 900 °C, 15 sec RTA. The specific contact resistance was calculated to be  $\approx 4.3 \times 10^{-1} \Omega \text{cm}^2$ , assuming a bulk resistance of zero for the underlying p-GaN. AES depth profiles showed widespread Cr diffusion through the Au layer to the surface. This metallization scheme also dissociated GaN with Ga diffusing both to the surface as well as forming a Au:Ga layer below the surface. At the metal/semiconductor interface, Cr, Ga, and N were present in an unidentified compound. High resolution XTEM showed a planar metal/semiconductor interface with no GaN surface segregation in the as-deposited condition. After the RTA, the interface was very rough. EDS was used to show that a Ga rich layer had formed at the surface of the contact following the RTA, consistent with the Ga segregation to the surface indicated by AES. Temperature dependent I-V characteristics were measured for the Ni/Au, Pd/Au, and Cr/Au contacts. Both Ni/Au and Pd/Au showed strong dependence of the current on the measurement temperature while the Cr/Au contacts showed no dependence of current on temperature, suggesting transport was dominated in the former two contact schemes by thermionic field emission, while field emission alone dominated in the case of Cr/Au contacts. The prospects for simple metallic schemes for low resistance ohmic contacts to p-GaN is not very promising.

**(IV) Degradation of ZnSe-Based LEDs (J. Kim, V. Krishnamoorthy and K.S. Jones)**

Light emitting diodes fabricated from II-VI materials typically have very short lifetimes. It has been suggested that the lattice mismatch strain in the multilayer structures employed in the fabrication of LEDs could be relieved by the formation of dislocations and these defects in turn cause the device to fail. The objective of this work was to understand the failure mechanism in such devices. An understanding of this mechanism could lead to improvements in device design which could help prolong the operating life of II-VI based LEDs.

Degradation studies were conducted on ZnCdSe quantum well structures with ZnSSe cladding layers. The LEDs were electrically degraded using the following conditions : current density=100A/cm<sup>2</sup>, repetition rate=10kHz and a duty cycle of 40%. The devices were degraded for times varying from 15 minutes to 1 hr. The samples were analyzed using Cathodoluminescence (CL) microscopy, Transmission Electron Microscopy (TEM) and Photoluminescence (PL).

The LEDs were degraded until the final output power decreased to 80%, 75% and 50% of the initial output power. EL microscopy analysis showed the evolution of dark line defects in each case. TEM analysis of these samples showed dislocations confined to the quantum well area of the sample. Dislocations seemed to emanate from the quantum well region and spread to the surrounding layers. Plan-view TEM analysis of these samples showed two sets of dislocation lines perpendicular to each other oriented along the <100> directions. These lines corresponded to the dark line defects (in terms of line spacing and orientation) observed by CL microscopy. These defects are believed to be responsible for device failure in II-VI LEDs. These dark line defects seemed to be comprised of smaller defect clusters that are connected along the <100> direction. This is the first time that dark line defects have been clearly distinguished in the TEM. Low temperature PL was performed to investigate changes in strain in the quantum well. The results showed no change in strain which suggests that defects due to strain relaxation are not the main cause of degradation in LEDs. Instead, we believe that point defects are generated in the quantum well region during LED operation. These defects coalesce into defect clusters and align themselves along the <100> directions. At this stage they are observable in CL and TEM and are termed dark line defects. Pre-existing defects such as stacking faults and dislocations may act as nucleation sites for these degradation-induced defects.

**(V) Microstructural Characterization of GaN Films Grown On LiGaO<sub>2</sub> Substrates by Metalorganic Chemical Vapor Deposition (Jing-Hong Li and Kevin S. Jones)**

One of the main problems in developing light emitting diodes and laser diodes materials is the crystalline quality of grown films which usually contain a high density of defects, including dislocations and stacking faults on the order of 10<sup>10</sup>/cm<sup>2</sup>. Optoelectronic properties, such as spatial luminescence may be correlated with the distribution of dislocations. Defects may decrease the efficiency of a device by acting as non-radiative recombination sites. One of major obstacles in improving crystalline quality of films is the lack of suitable substrates which are lattice and thermally matched to GaN. To optimize the GaN film growth and its optoelectronic properties, it is necessary to understand extended structural defects and other types of defects. Our objectives



are to characterize the microstructure of GaN films grown on the new substrate of LiGaO<sub>2</sub> by metalorganic chemical vapor deposition (MOCVD) along with characterization of the LiGaO<sub>2</sub> substrate itself using TEM and high resolution TEM (HRTEM), and to provide supporting information for processing.

The GaN films were grown on (001) LiGaO<sub>2</sub> substrates. The GaN films were deposited in one hour in a low pressure, horizontal cold-wall MOCVD reactor on the (001) LiGaO<sub>2</sub> substrate with triethylgallium and ammonia NH<sub>3</sub> as precursors and N<sub>2</sub> as carrier gas using a V/III ratio of 3324 and substrate temperature of 850°C under a reactor pressure of 130 Torr. The GaN films were typically 0.35-0.5 μm thick. Cross-sectional and plan-view TEM (XTEM and PTEM) analysis and HRTEM have been carried out on the GaN thin films. XTEM samples were prepared by first sticking two pieces of film face-to-face, cutting with a low speed saw, grinding to ~100 μm, dimpling down to 20 μm, and finally ion-beam milling from both sides. XTEM and HRTEM were carried in a JEOL 200C and a JEOL FX4000, respectively.

#### Crystalline Quality of the GaN Films and Threading Dislocations

TEM and selected area diffraction patterns (SADPs) have shown that the GaN film is single crystal in nature and grew epitaxially on the LiGaO<sub>2</sub> substrate with the following orientation relationship:  $[2\bar{1}\bar{1}0]_{\text{GaN}} \parallel [010]_{\text{LiGaO}_2}$ ;  $(0002)_{\text{GaN}} \wedge (002)_{\text{LiGaO}_2} < 5-8^\circ$ . The observed 5-8° misorientation between the GaN and the LiGaO<sub>2</sub> resulted from mis-cutting of the LiGaO<sub>2</sub> substrate.

The GaN films had high crystalline quality. The dislocation density of the GaN film was been measured to be about  $2.4 \times 10^8/\text{cm}^2$  from plan-view TEM images. The threading dislocation density was high near the interface, but it decreased with increasing distance from the interface. The dislocation Burger's vectors for some of the threading dislocations were determined to be  $[0001]$  and  $1/3[11\bar{2}0]$ . These dislocations are predominantly edge-type, assuming that the growth direction is the same as the translation vector of the dislocations.

#### GaN Stacking Faults and Inversion Domain Boundaries

In addition to the dislocations, stacking faults have been observed in the GaN films, causing streaking along the  $[0002]$  in the corresponding SADP of the GaN. The streaks were attributed to basal plane stacking faults which were parallel to the interface or the LiGaO<sub>2</sub>  $\{001\}$  planes. Near the GaN/LiGaO<sub>2</sub> interface, the GaN film has a higher density of stacking faults, with a decreasing density further from the interface. High densities of dislocations in the GaN are believed to result in nucleation sites for stacking faults.

Besides threading dislocations and stacking faults, columnar inversion domains have been found in GaN films and confirmed by convergent beam electron diffraction (CBED) patterns taken from two adjacent inversion domains. From the CBED patterns, we were able to identify the columnar defects are inversion domain boundaries (IDBs) where different domains show opposite contrasts when imaged with opposite diffraction reflections. HRTEM observations have confirmed the above conventional TEM results. IDBs are formed due to the atomic steps at the surface of a substrate. On one side of the IDB, the GaN is terminated with Ga orientated along  $[000\bar{1}]$ , while on the other side, the GaN is terminated with N orientated along  $[0001]$ . Furthermore, "house-shaped" inversion domains appear in the grown GaN films. In our HRTEM work, we found that the surface of the LiGaO<sub>2</sub> has some disordered region, producing some steps at surface. This is believed to contribute the formation of IDBs.

### GaN/LiGaO<sub>2</sub> Interface

TEM image contrast analysis showed that there was residual strain at the interface between the GaN and the LiGaO<sub>2</sub> substrate, even though the GaN and the LiGaO<sub>2</sub> had a very small mismatch of 1%, indicating that the lattice mismatch was not completely relieved by misfit dislocations. The interface of GaN/LiGaO<sub>2</sub> was quite rough. The XTEM micrographs and corresponding SADP revealed that there was an amorphous/nanocrystalline inter-layer between the GaN film and the LiGaO<sub>2</sub> substrate with a thickness of 50-100nm. The HRTEM micrographs also confirmed the above XTEM observations.

Two possible mechanisms of formation of the amorphous/nanocrystalline inter-layer have been analyzed. One is a possible interfacial reaction. The presence of the amorphous or nanocrystalline inter-layer indicates that there probably is a interfacial chemical reaction during the GaN film growth. This is critical to the crystalline quality of the GaN film since the amorphous or nanocrystalline region may change lattice mismatch, leading to a high density of threading dislocation, even though the GaN and the LiGaO<sub>2</sub> substrate have a very small lattice mismatch of 1%. This inter-layer might be formed during the film growth at high temperature because of inter-diffusion of N and Li or O, or reaction of the film and the substrate. We have found evidence of Li diffusion into GaN. This may lead to the formation a new interface phase, such as Li<sub>5</sub>GaO<sub>2</sub>. Another possibility is degradation of the surface of LiGaO<sub>2</sub> substrate due to poor chemical and mechanical polish of the substrate.

### Microstructures of LiGaO<sub>2</sub> Surface after Nitridation

The surface microstructure of a substrate is one of the most important factors in control of the crystalline quality of epitaxial films. Experimental results has shown that nitridation of a substrate's surface before completion of epitaxial growth by means of activated nitrogen leads to reconstruction of the surface and to improvement of the crystalline quality of the growth layer. So we carried out HRTEM characterization of nitridation of the surface of LiGaO<sub>2</sub>.

Cross-sectional HRTEM image revealed that there was a ~10-15 nm deep disordered region with a step height of 5-10 nm at the surface of as-received LiGaO<sub>2</sub> substrate. The high contrast in that region and the bending lattice images in the HRTEM images indicates that some degree of stress still remained in the disordered region. Below the disordered region, the LiGaO<sub>2</sub> showed high crystalline quality.

After an NH<sub>3</sub>-treatment, plan-view HRTEM images revealed random contrast and bending of lattice images, indicating that high strain remained in the LiGaO<sub>2</sub>. SADP from the NH<sub>3</sub>-treated LiGaO<sub>2</sub> did not show the existence of any other phase. But the corresponding HRTEM image did show some Moiré fringes, suggesting that there is another phase overlapping the LiGaO<sub>2</sub>. Cross-sectional HRTEM revealed that the disordered region observed in the as-received LiGaO<sub>2</sub> had disappeared. The surface of the LiGaO<sub>2</sub> exhibited an atomically flat surface structure with a step height of 0.5-1.0 nm. The lattices at the surface were bent with higher contrast as compared with the LiGaO<sub>2</sub> substrate, indicating either a change of lattice parameters of the LiGaO<sub>2</sub> or formation of another phase overlapping the LiGaO<sub>2</sub> (such as GaN). But, GaN has not been directly observed by HRTEM. This may be due to the fact that the NH<sub>3</sub>-treatment time of 10 min was not long enough to form GaN. Moreover, the surface of the NH<sub>3</sub>-treated LiGaO<sub>2</sub> became atomically flat with smaller steps as the NH<sub>3</sub>-treatment temperature increased. All of these results show that a



big improvement of the surface structure of the LiGaO<sub>2</sub> substrate has been achieved by NH<sub>3</sub>-treatment by reducing step height and eliminating the disordered region at the surface.

There are several mechanisms that correspond to the HRTEM observations about the improvement of surface structure after NH<sub>3</sub>-treatment. Improvement of the NH<sub>3</sub>-treated LiGaO<sub>2</sub> may come either from some chemical reactions in the surface region, or dissolution of N into the surface of LiGaO<sub>2</sub> without changing its crystal structure. The exact mechanism of improvement of the surface of LiGaO<sub>2</sub> is not very clear at present. Further work is required. Nevertheless, the nitridation of the surface of LiGaO<sub>2</sub> leads to the improvement of the surface structure of the substrate by using an NH<sub>3</sub>-treatment.

#### Summary:

In summary, plan-view and cross-sectional TEM and HRTEM microstructural characterization work have been carried out on the GaN films, the GaN/LiGaO<sub>2</sub> interface and surface of NH<sub>3</sub>-treated LiGaO<sub>2</sub> substrate. Our microstructural characterization work show that high crystalline quality of GaN films have been achieved with a dislocation density of  $2.4 \times 10^8/\text{cm}^2$ . In addition to dislocations, a high density of stacking faults and inversion domain boundaries have also been found in the GaN films. Dislocation and stacking fault densities are higher near the GaN/LiGaO<sub>2</sub> interface. An amorphous/nanocrystalline inter-layer has been found at the GaN/LiGaO<sub>2</sub> interface. Before nitridation, damaged, disordered region about 10-15 nm deep were found with some steps of 5-10 nm at the surface of LiGaO<sub>2</sub>. The surface of the LiGaO<sub>2</sub> was very rough. This may contribute to the formation of inversion domain boundaries in the MOCVD grown GaN film. After nitridation by NH<sub>3</sub>, the surface of LiGaO<sub>2</sub> became atomically flat with some small steps of 0.5-1.0 nm. Nitridation of the LiGaO<sub>2</sub> led to improvements of the surface structure of the LiGaO<sub>2</sub> substrate.

### **(VI) Optical and Electrical Characterization of ZnSe (Joseph Simmons)**

Our research effort has focused on (1) measuring and understanding the optical properties of wide-gap compound semiconductors, and (2) studying carrier dynamics.

- Development of high quality doped semiconductor structures were supported with high resolution photoluminescence spectroscopy measurements down to 10K, and room-temperature Raman measurements. By comparing the intensities of free exciton peaks with those from bound excitons and donor-acceptor peaks, we have identified the effect of substrate on growth condition, and assisted in the development of optimum growth conditions.
- Carrier dynamics in doped n and p-type ZnSe and GaN were measured and used to develop a model for the semiconductor-metal transition observed in these films.
- The majority-carrier mobility in n-type and p-type ZnSe was measured and modeled for its dependence on carrier-carrier interactions, impurity scattering and phonon scattering.
- Time-resolved photoluminescence capabilities were developed and used to measure carrier lifetimes in quantum well structures with resolution down to 100 femtoseconds.
- The carrier lifetimes in ZnSe quantum well structures were used to determine the role of carrier recombination processes in gain in lasers. Studies have shown that femtosecond

population-mixing measurements can reveal (a) accurate carrier lifetimes, (b) the influence of device structures on carrier-carrier interactions, and (c) the effect of current-induced damage on carrier behavior. Studies of structures with varied quantum well thickness and barrier width led to an analysis of exciton and bi-exciton lifetimes and revealed the role of carrier tunneling between adjacent wells. Continued measurements using this technique helped identify the source of non-radiative carrier decay associated with various device structure characteristics (barrier layer thickness, quantum well width/barrier layer thickness, etc.) and with exposure to the high current densities required of laser operation. Results were analyzed to suggest improvements in device structure characteristics and to calculate the associated cavity gain for various laser structures.

Formation and dynamics of excitons and biexcitons in ZnSe were identified and quantified. The process of bi-exciton formation was clearly identified as was the role of biexcitons in low temperature lasing in ZnSe. Photoluminescence data are shown in Fig. VI.1 as a function of excitation power. The exciton features are shown and are scaled to remain at constant intensity. The biexciton peak is also shown and it follows strict dependence on the square of the power of the excitation intensity.

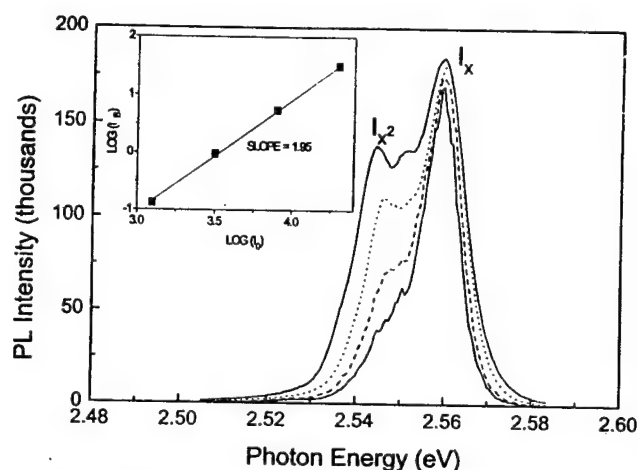


Fig. VI.1. 10 K PL spectra for various excitation intensities: 2.4, 1, 0.4 and 0.15  $\mu\text{J/pulse}$ . The curves are normalized to each other at the exciton peak and offset for clarity. Inset: plot of biexciton intensity vs the excitation intensity. The areas were calculated using double Gaussian fits to the luminescence data. The line is a linear fit of the data.

The role of high carrier densities in damage of ZnSe films, quantum wells, diode and laser structures was studied. The data show both current-induced damage and photo-current-induced damage. Both forms of damage were chosen to allow separation of the complex interactions of a device into its component parts and to allow isolation of the damage source and its failure characteristics. Measurements of damage with photoluminescence and population mixing spectroscopies was correlated with TEM. Our results showed the time and power dependence of high carrier damage in ZnSe quantum wells and their effects on photoluminescence and carrier lifetimes. Structural damage quenched luminescence and shortened carrier lifetimes, however the amount of damage appeared to saturate after about a 60% decrease in photoluminescence intensity. A damage model was developed and used to predict that if more gain could be designed in the ZnSe structures, the effect of structural damage on optical properties could be overcome.

## (VII) MOCVD Growth of Epilayers (Timothy J. Anderson)

The growth of wide bandgap II-S and III-N materials by metalorganic chemical vapor

deposition (MOCVD) was explored in this project. Growth of these materials was performed in three reactors; one commercial reactor for III-N growth, one customized reactor for hydride VPE growth of GaN, and a commercial reactor for growth of the group II sulfides.

### MOCVD Growth of ZnCdS

An exploratory research program was initiated to understand growth of  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  on GaAs leading to the possibility of growing the pseudoternary solid solution  $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{S}$ . The motivation for this work was the development of an alternative blue light emitter to the ZnSe-based chemistry. The advantages of this material system include: 1) lattice matching to GaAs over a wide range of bandgap energies, 2) simpler composition control since the solid solution is entirely on the group II sub-lattice, and 3) safer Se-free processing. Since no reports existed in the literature on this system, the pseudobinary system  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  was addressed first to gain experience. A summary of our research findings is given below.

Thin  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  films were grown on (100) and (111) oriented GaAs using diethyl zinc, dimethyl cadmium and  $\text{H}_2\text{S}$ . An extensive growth optimization study produced the lowest reported FWHM values of HRXRD peaks for  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  on GaAs (2000 and 500 arcsec for (100) and (111) GaAs, respectively).

The microstructure was dominated by a high density of stacking faults as suggested by surface energy considerations. Growth temperature, VI/II ratio, substrate orientation, buffer layer, growth rate, and substrate preparation procedures were studied to determine their effects on crystallinity.

High growth temperature consistently produced the best quality ZnCdS epilayers due to promotion of a 2-D growth, although the high vapor pressure of the system limited the growth temperature to below  $650^\circ\text{C}$ . The VI/II ratio also had a strong influence on the crystalline quality. In addition a lower growth rate produced better quality films due to increased residence time. A variety of substrate preparation procedures were tested and only an ammonia hydroxide etchant was shown to provide good quality epilayers. The growth of a ZnSe buffer layer prior to growth of ZnCdS was investigated, but this step did not give an improved microstructure.

The optical, physical and electrical properties of the films were also characterized. The bandgap energy for the entire compositional range of ZnCdS was determined for the first time by reflectance measurement and confirmed by PL measurement. The relationship between bandgap energy and solid phase composition fitted a quadratic expression with a bowing parameter typical of other II-VI systems. The bandgap energy at GaAs lattice matched conditions was 2.71 eV which is well within the blue and purple region of the visible spectrum.

The thermal expansion coefficients were calculated from measured lattice constants at various temperatures. The lattice constants were measured perpendicular to the growth surface along the  $\langle 004 \rangle$  direction by HRXRD. The results showed that the ZnCdS epilayer grown on GaAs was under compressive strain, although the thermal mismatch was not sufficient to produce a high density of strain induced dislocations.

The carrier concentrations with n and p-type doping were determined by Hall measurements. TEAl and TEGa were tested as n-type dopants. The results showed poor incorporation and activation extents with a maximum electron concentration of about  $10^{15} \text{ cm}^{-3}$ . A novel p-type dopant, bis-trimethyl silyl amido zinc, showed high resistivity with no measurable hole concentration. PL measurements indicated deep level optically active defects were introduced, most likely due to carbon contamination.

A model based on regular solution theory was developed to predict the solid vapor equilibrium (SVE) of ZnCdS at various temperatures. The model fitted the experimental data very well. For the first time, the interaction parameter between the binary constituent compounds have been calculated using Stringfellow's DLP model based specifically on material properties of II-VI compounds. The SVE model predicted the solid vapor equilibrium for ZnSSe with success.

A symmetric three layer slab waveguide (ZnCdS/ZnSe/ZnCdS) was fabricated and photopumped to assess the lasing capabilities of the active layer and the confining abilities of the cladding layer. Spectral narrowing and a sharp spectral line were not visible; an indication of a poor lasing medium and poor optical confinement. The peak position of the spectrum indicated that the ZnCdS was luminescing instead of the active layer, suggesting poor crystallinity of ZnSe grown on ZnCdS. A thin ZnCdS film grown on GaAs was also photopumped and again spectral narrowing was not observed.

Calculations were performed to determine the optical field distribution and optical confinement of a ZnCdS/ZnSe/ZnCdS waveguide. Results showed that the TE is the dominant mode. Increasing Cd composition in ZnCdS cladding, decreasing the active layer thickness, and higher mode order all decreased optical confinement. Calculations also showed that the minimal hole and electron carrier concentrations are roughly  $10^{18} \text{ cm}^{-3}$  to obtain population inversion and maintain stimulated emission.

The premature reactions between the metalorganics (DEZn and DMCd) and  $\text{H}_2\text{S}$  in the gas phase were believed to be responsible for the poor crystallinity. Low growth pressure and introduction of reactants through separate inlet lines were some of the precautionary measures taken to minimize parasitic gas phase reactions. Nevertheless it was believed that the parasitic reactions were a problem and an alternative deposition chemistry was investigated to decrease the reactivity.

$\text{H}_2\text{S}$  is a strong Lewis base and reacts with the group II metal alkyls, even at room temperature. The use of less reactive methyl mercaptan was explored. The use of this source for the growth of the more extensively studied ZnS on Si was explored. A FWHM of 350 arcsec was measured when the growth temperature was  $600^\circ\text{C}$ , the II/VI ratio was 60 and the growth rate was 1 mm/hr. SIMS analysis indicated no increase in C incorporation with the use of methyl mercaptan when compared to  $\text{H}_2\text{S}$ . Thus, this source is promising and merits further investigation.

### MOCVD Growth of GaN

The growth of GaN by MOCVD was investigated using a conventional chemistry (TEGa and  $\text{NH}_3$ ) as well as a merged hydride-MO chemistry (TMGa, HCl,  $\text{NH}_3$ ). The research objective with the conventional chemistry was to lower the growth temperature to  $<850^\circ\text{C}$  with a view towards efficient In incorporation. For the merged hydride-MO chemistry the goal was to grow very thick GaN films for eventual substrate use.

The first effort was a parametric study of GaN growth using sapphire (a, c and r orientations) and a low temperature buffer layer (conventional approach). An optimization of the buffer layer growth process, growth rate, temperature and Ga/N ratio produced films with very respectable quality (FWHM  $\sim 200$  arcsec) given the low growth temperature ( $800^\circ\text{C}$ ). The quality of these films, however, were inferior to those grown at high temperature ( $1050^\circ\text{C}$ ). The low rate of thermal decomposition of  $\text{NH}_3$  at the lower growth temperature was believed to be the primary obstacle. Our first approach to increase the rate of  $\text{NH}_3$  decomposition was to investigate

the use of known catalysts. Wafers patterned with SiO<sub>2</sub>, Mo, W, and TiC were tested with the idea that these materials would locally enhance the decomposition of NH<sub>3</sub> with subsequent N radical spillover. The results of these selective area deposition experiments indicated a growth rate enhancement, but the eventual poisoning of the catalyst through nitride formation led to their degradation with time.

Our next approach was to explore alternative substrates including SiC, LiAlO<sub>2</sub> and LiGaO<sub>2</sub>. Considerable success was achieved with this latter substrate and the key results are summarized below.

Films grown of LiGaO<sub>2</sub> and LiAlO<sub>2</sub> using H<sub>2</sub> as the carrier gas produced films of poor structural quality as determined by HRXRD. The films grown in an H<sub>2</sub> ambient exhibited a double axis FWHM for the (0002) reflection of GaN of 4200 to 4500 arcsec. SEM micrographs of substrates treated with H<sub>2</sub> showed that surface had degraded the LiGaO<sub>2</sub> and LiAlO<sub>2</sub> at temperatures as low as 550°C. The subsequently grown GaN nitride films had a granular texture with a measured AFM surface roughness on the order of 1 μm consistent with a 3-D growth mechanism. The H<sub>2</sub> apparently reduced the substrate surface prior to the initiation of growth and the reduction products or rough surface produced a 3-D growth mechanism.

A series of experiments were next conducted by exposing the oxide substrates to N<sub>2</sub> at various temperatures. It was observed that no surface degradation occurred. Subsequent films grown in N<sub>2</sub> or LiGaO<sub>2</sub> at 850°C exhibited excellent surface and crystalline quality. The FWHM of films grown in N<sub>2</sub> were more than an order of magnitude lower (<160 arcsec) than those grown in H<sub>2</sub>. For growth on LiAlO<sub>2</sub>, however, inconsistent film quality was observed and possibly related to the quality of the substrate.

It was next discovered that NH<sub>3</sub> pretreatment had a significant effect on the quality of the subsequently grown GaN, which were deposited in a low pressure horizontal cold-wall MOCVD reactor with triethylgallium (TEGa) and ammonia (NH<sub>3</sub>) as precursors and N<sub>2</sub> as the carrier gas at substrate temperature between 650 and 900°C, V/III ratio = 3000, and a reactor pressure of 100 Torr. Substrates were pre-heated in nitrogen (N<sub>2</sub>) for 10 min at 850°C before nitridation in the reactor. This was followed by a nitridation step using NH<sub>3</sub> (1500 sccm). The exposure to NH<sub>3</sub> varied from 30 s to 10 min. Thin GaN layers were grown on the nitrided substrate surface using a growth time of 1 min (estimated thickness 85 to 100 Å). The surface morphology of the pretreated substrate prior to growth was determined by AFM and the chemical composition analyzed by AES. The results are shown in the table below.

RMS surface roughness and N content of treated LiGaO<sub>2</sub> surfaces

| Treatment                | R <sub>g</sub> (nm) | Content (at.%) |
|--------------------------|---------------------|----------------|
| as-received              | 3.40                | not detected   |
| 650°C (NH <sub>3</sub> ) | 0.58                | 2.49           |
| 800°C (NH <sub>3</sub> ) | 0.12                | 6.31           |
| 900°C (NH <sub>3</sub> ) | 0.10                | 8.61           |
| 650°C (N <sub>2</sub> )  | 3.8                 | not detected   |
| 800°C (N <sub>2</sub> )  | 3.6                 | not detected   |
| 900°C (N <sub>2</sub> )  | 3.2                 | not detected   |



ESCA spectra for the  $\text{NH}_3$  treated substrates surfaces showed chemical shifts for the Ga3d peak indicated that Ga-N bonds formed a Li-Ga-O-N compound likely formed in the near surface regions.

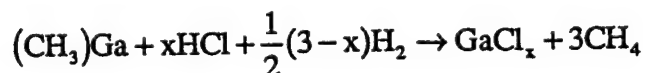
There was also concern that Li diffusion into the GaN film would deteriorate the electrical properties of the material. Using SNMS Li profiles were measured in GaN films. These data indicate a significant difference in the value of the lithium diffusion coefficient, depending on the substrate pretreatment. In particular, when the substrate was pretreated with  $\text{NH}_3$  the lithium diffusion coefficient was very small and decreased from  $(5 \pm 3) \cdot 10^{-17}$  to  $(6 \pm 2) \cdot 10^{-18} \text{ cm}^2/\text{sec}$  as the substrate pretreatment time decreased from 10 min to 30 sec.

A simple thermodynamic analysis of nitridation of the binary oxides  $\text{Ga}_2\text{O}_3$  and  $\text{Li}_2\text{O}$  indicated preferential formation of GaN compound to  $\text{Li}_3\text{N}$ . However, mixed oxides or more complex nitride complex could also be formed. The results obtained by AES and SNMS show that nitridation of the surface of (001)  $\text{LiGaO}_2$  leads to formation of either GaN or a mixed Li-Ga-O-N compounds in the 50/100 Å surface layer of the substrates. There is no evidence of nitrogen incorporation in the case of nitrogen pretreatment at the same temperature.

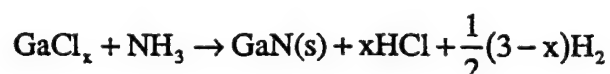
The microstructure of the near surface region of as-received and nitrided  $\text{LiGaO}_2$  substrate was analyzed by HRTEM. Before nitridation an approximately 10-15 nm deep disordered region was formed at the  $\text{LiGaO}_2$  surface. High contrast in that region indicated that some degree of stress still remained in the disordered region. After  $\text{NH}_3$  treatment the disordered region observed for as-received  $\text{LiGaO}_2$  disappeared and the  $\text{NH}_3$ -treated surface exhibited a high degree of crystalline quality. Atomically flat surfaces were observed with steps less than 5 Å measured. The lattice images at surface were bent with a higher contrast compared to the  $\text{LiGaO}_2$  indicating either a change in lattice parameters of the  $\text{LiGaO}_2$  or formation of another phase.

The nitridation of  $\text{LiGaO}_2$  substrates prior to GaN growth had a peculiar and positive effect. It is believed that a surface reaction product is formed that promotes recrystallization of the underlying  $\text{LiGaO}_2$  and shows a lattice parameter very close to that of GaN. Furthermore, this reaction product serves as an efficient barrier for Li transport into the GaN. The quality of the GaN grown on the pretreated  $\text{LiGaO}_2$  substrates was remarkably high. The surfaces were atomically flat, and the bulk microstructure was excellent as judged by TEM micrographs and HRXRD analysis. Indeed, FWHM of the order of 25 arcsec was observed, although the interpretation of the spectrum is still under consideration. In summary,  $\text{LiGaO}_2$  is a very promising substrate for the growth of high quality GaN. The main unresolved issue is the ability to grow larger diameter bulk crystals of  $\text{LiGaO}_2$ .

A novel technique for the deposition of gallium nitride was explored that combines the advantages of MOCVD and hydride VPE. In this process, trimethylgallium (TMGa) is first reacted with HCl in the source zone of a hot wall reactor to form chlorinated gallium species according to the following reaction:



This stream is then combined with  $\text{NH}_3$  in the downstream mixing zone and passed over a substrate where deposition of GaN occurs by the following reaction:



The advantages of this technique include high growth rate (~ 100 times that observed in MOCVD), high purity (the Cl retains metal impurities in the vapor phase), and the easy source delivery associated with MOCVD.

The first problem was to determine the conditions necessary for formation of GaCl from TMGa and HCl. The reaction of TMGa with HCl to produce GaCl was expected to occur within a narrow temperature range. The upper bound is set by the decomposition temperature of TMGa since decomposition before the reaction with HCl would yield liquid gallium wall deposition. If the temperature is too low an adduct compound will form between the HCl and TMGa and furthermore the formation of gallium trichloride ( $\text{GaCl}_3$ ) is thermodynamically favored over the monochloride (GaCl).  $\text{GaCl}_3$  is a liquid and gives inefficient growth. The key then was to determine the location and temperature at which the HCl should be mixed with the TMGa stream. This temperature was determined to be in the range of 250 to 350°C and under this condition GaN could be grown at high deposition rates (~ 40 nm/hr).

Films were grown at temperatures ranging from 450°C to 975°C, at HCl/Ga ratios from 0 to 12, and at  $\text{NH}_3$  flows from 100 to 500 sccm. The surface features of films grown at 900°C included hexagonal pyramids and mesas, as observed on conventional hydride films. The smoothest films had feature sizes of approximately 50 nm, as measured by stylus profilometer. In contrast conventional hydride films have reported surface roughness on the order of microns. Lateral and longitudinal uniformity were also improved with deposition technique. The most uniform merged hydride films were uniform to  $\pm 3$  mm across 1 cm x 1 cm substrate, which is significantly better than the 20% results for conventional hydride.

The growth rate was measured in the range 500 to 950°C. Growth was reaction-limited below 750°C, and diffusion-limited above this temperature.

The variation of the growth rate with HCl/Ga ratio was also studied at 750°C. At an HCl flow rate of zero, the growth rate was low, typical of MOCVD growth. As HCl was added the rate increased and proceeded through a maximum near equimolarity, after which it tailed off to zero with high excesses of HCl. This is consistent with thermodynamic predictions and conventional hydride results which demonstrate lower growth rates with increased HCl concentration.

The growth rate was found to be independent of the  $\text{NH}_3$  flow rate for V/III ratios > 100. Qualitatively, films grown with higher  $\text{NH}_3$  flow rates appeared smoother, and films seemed less prone to cracking with higher  $\text{NH}_3$  concentrations.

Films were characterized for microstructure by HRXRD. As an example, a FWHM of 600 arcsec for the (002) reflection of GaN was observed for a film grown at 950°C on c-oriented sapphire without a low temperature buffer layer. The FWHM for a film grown by MOCVD (without HCl) under the same conditions was about twice that observed for the chloride based chemistry.

The best hydride films showed an intrinsic n-type carrier concentration of  $1.5 \times 10^{18} \text{ cm}^{-3}$  (FTIR), which is consistent with literature results for hydride VPE. SIMS analysis of both hydride and MOCVD films grown in the merged-hydride reactor showed the presence of Cl, C, and O. Comparative analyses showed that the film grown with the merged hydride technique incorporated more chlorine than the standard MOCVD technique, but more importantly, incorporated less carbon and oxygen.

The merged hydride technique for the chemical vapor deposition of gallium nitride has proven to be a technology with potential for the growth of high quality gallium nitride film,

particularly for applications which require thick films. Growth rates comparable to conventional hydride VPE have been achieved for single-crystalline film using metalorganic reactants. Crystalline quality for as-grown films proved superior to conventional MOCVD for films grown in the same reactor, and comparable to FWHM values found in the literature.

### **(VIII) CdZnSe Quantum Well (QW) Diode Lasers (Peter Zory)**

The lasing process in CdZnSe QW diode lasers was successful in simulating the measured spectral gain and absorption features of room-temperature without using "excitons". As is well known in the semiconductor laser community, it had been publicized that spectral features due to excitonic gain and absorption dominated in room temperature CdZnSe. In our model, the absorption features were due to collective excitations of the electron hole plasma, not excitons. The key to success was to learn how to incorporate Coulomb attraction effects into conventional semiconductor laser theory.

On the experimental side, we collaborated with Michael Haase of 3M who has provided us with state-of-the-art material for laser fabrication and testing. In late May, we packaged and characterized a number of wide stripe CdZnSe lasers and demonstrated them to Air Force personnel at the Phillips Research Labs in Albuquerque, NM. While the half-life of the devices at high power levels was only about 15 minutes, there are Air Force applications where relatively short lifetimes are acceptable.

### **InGaN QW LED Material**

It was demonstrated that p-GaN and InGaN layers in high quality LED material grown at Xerox Palo Alto Research Center could be etch removed in minutes using a pulsed electrochemical technique. Movement of the etch front through the p-n junction region was observed by monitoring changes in the current pulse shape on an oscilloscope.

### **(VII) Theory of Doping in ZnSe and GaN (Gertrude F. Neumark)**

We have analyzed two aspects of the problems of heavily doped semiconductors, and have obtained major results in both.

One aspect was analysis of the difficulties in obtaining good bipolar conductivity, and we have shown that in cases of difficult doping, non-equilibrium dopant incorporation appears to be required. This result has been shown to apply, specifically, to both ZnSe:N and GaN:Mg [for details, see Kuskovsky and Neumark, Proc. 23 Int. Conf. On Compound Semiconductors, and Neumark, Materials Letters 30, 131 (1997)].

The second aspect involved the effect of (strong) potential fluctuations, present in heavily doped and compensated semiconductors (due to a Poisson distribution in the ionized impurities), on the photoluminescence (PL) properties [for details on the steady-state PL, see Kothandaraman, et al., J. Cryst. Growth 159, 298 (1996)]. In recent work, we have carried out a quantitative analysis, starting from the basic physics, of the effect of the fluctuations on the time decay of PL; the results provide a quantitative measure of the strength of the fluctuations, and thus of the extent of compensation. This work has been submitted to Phys. Rev. Lett. (Kuskovsky, et al.).



## Theses and Dissertations:

### PhD Degrees:

- "Dislocations at lattice mismatched widegap II-VI/GaAs heterointerfaces as laser light scatterers: Experiment and theory," Christopher M. Rouleau, PhD, University of Florida, Department of Materials Science and Engineering, Gainesville, FL, Aug. '94,
- "Molecular beam epitaxial growth of homoepitaxial ZnSe," Minhyon Jeon, PhD, University of Florida, Department of Materials Science and Engineering, Gainesville, FL, Dec. '95.
- "Impact of the growth kinetics on deep level defect production in GaN films grown by MBE," Hsing-Long Liu, PhD, University of Florida, Department of Materials Science and Engineering, Gainesville, FL, Dec. '96,
- "Processing Modules for GaN Devices," C. Vartuli, Ph.D. University of Florida, Department of Materials Science and Engineering, Gainesville, FL, 1996.
- "Formation and Characterization of Electrical Contacts to p-type ZnTe and GaN", J.T. Trexler, University of Florida, Department of Materials Science and Engineering, Gainesville, FL, August, 1997.
- "Electrical Contacts to p-Type Zinc Selenide," John J. Fijol, PhD, University of Florida, Department of Materials Science and Engineering, Gainesville, FL, 1996.
- "Carrier Dynamics Study of ZnSe and ZnSe Based Quantum Well Structures by -Using Time-Resolved Spectroscopy," Li Wang, PhD, University of Florida, Department of Materials Science and Engineering, Gainesville, FL, 1995.
- Y.S. Park - "A Study of the Electronic and Optical Properties of Visible Strained Quantum Well Diode Lasers", PhD, University of Florida, Department of Electrical Engineering, Gainesville, FL, 5/94.
- C.L. Young - "Temperature Dependence of Light Emission From Quantum Well Structures", PhD, University of Florida, Department of Electrical Engineering, Gainesville, FL, 1995.
- C.F. Hsu - "Many-Body Effects in II-VI and III-V Quantum Well Lasers", PhD, University of Florida, Department of Electrical Engineering, Gainesville, FL, 1997.
- J. Cho, "MOCVD Growth of ZnCdS", PhD, University of Florida, Department of Chemical Engineering, 1995.
- Z. Osman, "MOCVD Growth", PhD, University of Florida, Department of Chemical Engineering, 1995.
- C. McCreary, PhD, University of Florida, Department of Chemical Engineering, expected 1998.
- E. Brettschneider, "MOCVD of ZnSe", PhD, University of Florida, Department of Chemical Engineering, expected 1997.
- T. Dann, "MOCVD Growth", PhD, University of Florida, Department of Chemical Engineering, expected 1998.
- M. Reed, "MOCVD of GaN", PhD, University of Florida, Department of Chemical Engineering, PhD expected 1998.

#### MS Degrees:

- Jong-Jin Kim, MS, April '94, "Growth by MBE and electrical characterization of Si-doped zincblende GaN films deposited on -SiC coated (001) Si substrates."
- Lynn Calhoun, MS, Aug '94, "*In situ*, real-time determination of optimum growth conditions using cathodoluminescence for the MBE growth of nitrogen-doped p-type ZnSe."
- Austin Frenkel, MS, Aug. '95, "Growth by RF-plasma MBE and *in situ* characterization of InN and InGaN films."
- Jeffrey Trexler, Non-thesis MS, 1995.
- Suman Subramanian, Non-thesis MS, 1995.

#### BS Degrees:

Julie Sauer

#### Awards Received During Project Period

- Robert M. Park; 1996 University of Florida Excellence in Classroom Teaching Award (TIP Award).
- Robert M. Park; 1993 Rank Prize for Opto-Electronics (London, Nov. 1993).
- Christopher M. Rouleau; MRS Graduate Student Award - Fall '93 Meeting (Boston, Nov/Dec 1993).
- Paul H. Holloway, Fellow, American Vacuum Society, 1992,
- Paul H. Holloway, Professional Excellence Program Award, 1996.
- Paul H. Holloway, University of Florida Research Foundation Professor, 1997.
- Peter Zory, IEEE/LEOS Distinguished Lecturer, 1995-1996.
- Joseph Simmons, Professional Excellence Program Award, 1996.
- Kevin S. Jones, Promoted to Full Professor, UF, 1997.
- Stephen Pearton, Fellow of the Electrochemical Society, 1997.

#### Books:

GaN and Related Materials, ed. S.J. Pearton (Gordon & Breach, New York 1997).

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- C.M. Rouleau and R.M. Park "*In situ* real-time diffuse optical reflectivity measurements during GaAs cleaning and subsequent ZnSe/GaAs heteroepitaxy," J. Vac. Sci. Technol. A, **11**, 1792 (1993).
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- R.M. Park, "ZnSe homoepitaxy," DARPA/ONR Meeting, Crystal City, VA, Oct. 12-13, 1994.
- R.M. Park, "High mobility cubic GaN," Second Annual III-V Nitride Workshop, St. Louis, MO, Oct. 17-18, 1994 - INVITED.
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- "Conduction Mechanisms in W and SWi<sub>x</sub> Ohmic Contacts to InGaN and InN," C. Vartuli, S.J. Pearton, C.R. Abernathy, J. MacKenzie, M. Lovejoy, R. Shul, J. Zolper, A. Baca, K. Jones and F. Ren, 1997 Spring MRS Meeting, San Francisco, April 1997.
- "ICP Dry Etching of III-Nitrides," C. Vartuli, J. Lee, J. MacKenzie, C.R. Abernathy, S.J. Pearton, R.J. Shul, A. Katz, A.Y. Polyakov and M. Shin, 1997 Spring MRS Meeting, San Francisco, April 1997.
- "Er Incorporation and Optical Activity in III-V Nitrides Grown by MOMBE," J. MacKenzie, C.R. Abernathy, S.J. Pearton, U. Hommerich, F. Ren, R.G. Wilson and J.M. Zavada, 1997 Spring MRS Meeting, San Francisco, April 1997.
- "Substrate Effects on Growth of InN," S. Donovan, J. MacKenzie, C.R. Abernathy, P. Holloway, F. Ren, J. Zavada and B. Chai, 1997 Spring MRS Meeting, San Francisco, April 1997.
- "RTP of III-Nitrides," J. Hong, J. Lee, C. Vartuli, J. MacKenzie, S. Donovan, R. Crockett, C.R. Abernathy, S.J. Pearton, J. Zolper and F. Ren, 1997 Spring MRS Meeting, San Francisco, April 1997.
- "Technological Issues for Application of Group III-Nitride Semiconductors to High Temperature and high Power Electronics," J.C. Zolper, R.J. Shul, S.J. Pearton and F. Ren, 2<sup>nd</sup> Workshop on High Temp. Power Electronics for Vehicles, Adelphi, MD, April 1997.
- "High Density Plasma Etching of Wide Bandgap GaN," R.J. Shul, G.B. McClellan, S.J. Pearton, C.B. Vartuli and J.W. Lee, Surf. Analysis '97, Albuquerque, NM, May 1997.
- Li, J. H., Kryliouk, O., Holloway, P., Anderson, T. J., Jones, K. S., "Microstructures of GaN Thin Films Grown on A New LiGaO<sub>2</sub> Substrate By Metalorganic Vapor Deposition", 1997 MRS Meeting, San Francisco, CA, 1997

### Presentations-continued:

- "Comparison of Ni/Au, Pd/Au, and Cr/Au Metallizations for Ohmic Contacts to p-GaN" J.T. Trexler, S.J. Pearton, P.H. Holloway, M.G. Mier, K.R. Evans, and R.F. Karlicek, 1996 Fall Meeting of the MRS, Dec.2-6, 1996, Boston, MA.
- "Interfacial Reactions Between Metal Thin Films and p-GaN" J.T. Trexler, S.J. Miller, P.H. Holloway and M.A. Khan, 1995 Fall Meeting of the MRS, Nov.27-Dec 1, 1995, Boston, MA.
- "Reactions between Au/Ni Thin Films and p-GaN" J.T. Trexler, S.J. Miller, P.H. Holloway, and M.A. Khan, 42nd Annual American Vacuum Society National Symposium, October 16-20, 1995, Minneapolis, MN.
- "Ohmic Electrical Contacts to p-ZnTe" J.T. Trexler, J.J. Fijol, and P.H. Holloway, 41st Annual American Vacuum Society National Symposium, October 24-28, 1994, Denver, CO.
- "Ohmic Electrical Contacts to p-ZnTe" J.T. Trexler and P.H. Holloway, 23rd Annual Symposium of the Florida Chapter of the American Vacuum Society, February 6-8, 1995, Clearwater Beach, FL.
- "Characteristics of ZnSe Light Emitting Diodes as a Function of Temperature," Y. Guan, L. Calhoun, R.M. Park and P.S. Zory, Conference on Compact Blue-Green Lasers, Santa Fe, NM (February, 1992).
- "Temperature Dependence of the Threshold Current Density of CdZnSe Blue-Green Quantum Well Diode Lasers," Young-Soh Park and P.S. Zory, Proceedings of the IEEE/LEOS '93 Annual Meeting, San Jose, CA, (November 1993).
- "Coulomb Enhancement in CdZnSe Single Quantum Well Lasers," C.F. Hsu, P.S. Zory, P. Rees, and M. Haase, SPIE Photonics West, San Jose, CA (February 1997).
- "Pulsed Electrochemical Etching of InGaN/GaN LED Material", Jeongseok O and P.S. Zory and D.P. Bour, SPIE/Photonics West, San Jose, CA (February 1997).
- "Anomalous Temperature Dependence of Light Emission from CdZnSe MQW LEDs", P.S. Zory, 3M, St. Paul, MN, Oct. 1992.
- "Visible Semiconductor Lasers", P.S. Zory, half day course at OSA/IEEE sponsored Conference on Lasers and Electro Optics (CLEO), Baltimore, MD, May, 1993. (Invited)
- "Visible Semiconductor Lasers", P.S. Zory, organized and chaired session at IEEE/LEOS sponsored Semiconductor Laser Workshop, Baltimore, MD, May, 1993.
- "II-VI Diode Lasers - Design and Processing", P.S. Zory, organized and chaired Part of II-VI Laser Workshop at Gainesville Meeting, May, 1993.
- "Red/Blue-Green Quantum Well Lasers - a Comparison", P.S. Zory, Philips Laboratories, Briarcliff Manor, NY, 9 June 1993. (Invited)
- "Strained Quantum Well Lasers - Red and Blue-Green", P.S. Zory, Naval Air Warfare Center, China Lake, CA, 20 July 1993. (Invited)
- "II-VI vs III-V - which will win the Blue-Green Diode Laser Reliability Race", P.S. Zory, Panel Discussion of IEEE/LEOS Summer Topical Meeting, Santa Barbara, CA, 22 July 1993.
- "Blue-Green Diode Laser Overview", P.S. Zory, IEEE/LEOS Annual Meeting, San Jose, CA, 17 November 1993. (Invited)

### **Presentations-continued:**

- "Blue-Green Diode Laser Overview", P.S. Zory, Naval Research Laboratory, Washington, D.C. January, 1994. **(Invited)**
- "Blue-Green Diode Laser Overview", P.S. Zory, Boston University, Boston, MA, December, 1993. **(Invited)**
- "Blue-Green Diode Laser Overview", P.S. Zory, at the DOD/DOE sponsored Diode Laser Technology Conference in Fort Walton Beach, FL on 21 April 1994. **(Invited)**
- "Visible Semiconductor Lasers", P.S. Zory, short course at the OSA/IEEE sponsored Conference on Laser and Electro-Optics (CLEO), Anaheim, CA 10, 12 May 1994. **(Invited)**
- "Relative merits of II-VI and III-V wide bandgap light emitters" P.S. Zory, Eleventh Annual IEEE/LEOS sponsored Semiconductor Laser Workshop in Anaheim, CA, 13 May 1994.
- "URI Review talk", P.S. Zory, Arlington, VA. - 13 October 1994.
- "Blue-Green Diode Laser Overview", P.S. Zory, Kodak, Rochester, N.Y. - 14 October 1994. **(Invited)**
- "Blue-Green Semiconductor Lasers" P.S. Zory, at the 15th Winter Colloquium on Quantum Electronics - Snobird, Utah - 4 January 1995. **(Invited)**
- "Blue-Green Diode Lasers: Technology Status" P.S. Zory, at the Spring Meeting of the Materials Research Society - San Francisco, CA - 17 April 1995. **(Invited)**
- "Blue-Green Diode Lasers for Optical Memory Applications", P.S. Zory, Press Conference at the MRS Meeting (see above). **(Invited)**
- "Quantum Well Lasers" P.S. Zory, at the IEEE Princeton/Sarnoff Symposium - Princeton, N.J. - 28 April 1995. **(Invited)**
- "Visible Semiconductor Lasers", P.S. Zory, Short Course Conference on Electro-Optics and Lasers - Baltimore, MD - 25 May 1995. **(Invited)**
- "URI Review Talk", P.S. Zory, Big Sky, Montana, 3 August 1995.
- "Diode Laser Material Evaluation Using Liquid Contact Luminescence", P.S. Zory, C.L. Young, C.F. Hsu, J.S. O and C.C. Largent, IEEE/LEOS >95 Annual Meeting, San Francisco, CA, November 1995.
- "Coulomb Attraction Effects in CdZnSe Quantum Well Lasers", P.S. Zory, C.F. Hsu, P. Rees, and M.A. Haasse, IEEE/LEOS Summer Topical Meeting on GaN Materials, Processing and Devices, Montreal, Canada (August 1997).
- Panelists for "Critical Issues for Commercially Viable GaN Lasers", P. Zory with I. Akasaki, S. Nakamura, N. Johnson, Y.S. Park and A. Nurmikko, at the IEEE/LEOS Summer Topical Meeting on GaN to be held in Montreal, CN in mid-August, 1997.
- "Blue-Green Diode Lasers", P.S. Zory, IEEE/LEOS Distinguished Lecturer Series, Presented at following locations on these dates:
  - August 8, 1995 - University of Queensland in Brisbane, Australia
  - August 9, 1995 - Queensland University of Technology in Brisbane
  - August 11, 1995 - University of Western Australia in Perth
  - August 14, 1995 - University of Melbourne in Melbourne
  - August 16, 1995 - University of New South Wales in Sydney
  - August 18, 1995 - The Australian National University in Canberra

**Presentations-continued:**

September 22, 1995 - University of Toronto in Toronto, Canada  
September 25, 1995 - National Research Council in Ottawa, Canada  
September 28, 1995 - Sarnoff Research Council in Ottawa, Canada  
October 17, 1995 - University of Maryland in College Park, MD  
October 19, 1995 - NASA Langley in Norfolk, VA  
October 20, 1995 - Old Dominion University in Norfolk, VA  
November 2, 1995 - University of California in Davis, CA  
December 14, 1995 - MIT Lincoln Labs in Lexington, MA  
January 26, 1996 - Oregon Graduate Institute in Portland OR  
March 18, 1996 - University of Central Florida in Orlando, FL  
March 25, 1996 - City University in London, England, UK  
March 27, 1996 - University of Manchester in Manchester, England, UK  
April 1, 1996 - University of Wales, Cardiff, Wales, UK  
April 15, 1996 - University of New Mexico in Albuquerque, NM  
April 17, 1996 - Los Alamos National Laboratory in Los Alamos, NM  
April 22, 1996 - University of Texas in Arlington, TX  
April 23, 1996 - Southern Methodist University in Dallas, TX  
May 6, 1996 - University of Wisconsin in Madison, WI

**Post Doctoral Associates:**

Jing Hong Li with Dr. Jones  
Olga Kryliouk with Dr. Anderson  
A. Ahmed with Dr. Anderson  
A. Davydov with Dr. Anderson  
G. Alameddin with Dr. Anderson  
O. Kryliouk with Dr. Anderson  
O. Romulo Ochoa with Dr. Simmons  
Dr. Wafaa Gobba with Dr. Simmons  
Dr. Rajiv Bendale with Dr. Simmons

**Graduate Students Supported:**

Christopher Rouleau with Dr. Park  
Hsing-Long Liu with Dr. Park  
Minhyon Jeon with Dr. Park  
Lynn Calhoun with Dr. Park  
Austin Frenkel with Dr. Park  
Jong-Jin Kim with Dr. Park  
Jin Hong with Dr. Pearton

**Graduate Students Supported: - Continued**

Cathy Vartuli with Dr. Pearton  
K.N. Lee with Dr. Abernathy  
Li Wang with Dr. Simmmons  
Suman Subramanian with Dr. Simmons  
Julie Sauer with Dr. Simmons  
Joshua Greenberg with Dr. Simmons  
Youngsoh Park with Dr. Zory  
Chi-Lin Young with Dr. Zory  
Chia-Fu Hsu with Dr. Zory  
Jeong-Seok O with Dr. Zory  
John Fijol with Dr. Holloway  
Jeff Trexler with Dr. Holloway  
Joe Cho with Dr. Anderson  
Eric Brettschneider with Dr. Anderson  
Z. Osman with Dr. Anderson  
C. McCreary with Dr. Anderson  
T. Dann with Dr. Anderson  
M. Reed with Dr. Anderson